

## DESCRIPTION

### CATALYSTS AND PROCESS FOR THE DIRECT CONVERSION OF METHANE INTO ACETIC ACID

#### (a) Background, objective and advantages

The conversion of methane in valuable functionalised products constitutes one of the great challenges to modern Chemistry and, in particular, the catalytic synthesis of acetic acid from that gas and carbon monoxide has attracted a current high interest. For this process, a few catalysts based on vanadium oxides or heteropolyacids have been recently found [1], whereas a lower catalytic activity or selectivity has been recognized for other systems of  $\text{Pd}(\text{OAc})_2/\text{Cu}(\text{OAc})_2$  [2],  $\text{CaCl}_2$  [3],  $\text{NaVO}_3$  [4],  $\text{RhCl}_3$  [5,6] (in the presence of  $\text{O}_2$  [6] with formation also of formic acid and methanol), lanthanide salts [7],  $\text{K}_2\text{S}_2\text{O}_8$  [8] or superacids [9].

Moreover, the synthesis of carbonylated products without requiring the use of the noxious carbon monoxide is also of high interest and recently the conversion of methane into methyl trifluoroacetate or methyl acetate has been achieved by using vanadium heteropolyacids [10] or  $\text{Cu}(\text{OAc})_2$  [11] catalysts. Alternative processes for the conversion of methane into acetic acid by carbonylation of the former by carbon dioxide are also known in heterogeneous catalysis at temperatures in the 100-500 °C range, with Pd [12], Rh [13], Ir [13], Ru [13] or Cu/Co [14,15] catalysts, and they can involve two distinct stages with methanol as an intermediate [16].

The invention under consideration aims to select catalysts and establish a process for the single-pot direct conversion of methane into acetic acid, preferably without the use of carbon monoxide as the carbonylating agent, under mild or moderate temperature and pressure conditions.

Such catalytic systems would present high advantages, in terms of simplicity and energy saving, over the industrial process that is currently followed and involves three distinct complicated and energy expensive stages, *i.e.* (i) the steam reforming of methane (highly endothermic process, catalysed by a metal catalyst) to form the "synthesis gas", (ii) the catalytic conversion of this gas, also at high temperature, in methanol, and (iii) the carbonylation of this alcohol by carbon

monoxide to give acetic acid, usually by the Monsanto process which requires an expensive catalyst (based on rhodium or iridium in a BP-Amoco modified route). The invention in analysis uses a catalyst of vanadium, a much cheaper metal than those above.

### (b) Innovatory features

The invention relates to the establishment of new catalytic systems, active under mild or moderate operational conditions, for the direct single-pot conversion of methane into acetic acid, with considerable yields, particularly without the use of carbon monoxide, in contrast with the above methane carbonylating systems.

The inspiration on biological systems for the composition of some of the catalysts is also innovative, in particular by using models of Amavadine, a natural vanadium complex that exists in some Amanita fungi, whose biological function is still unknown. The invention extends, to the carbonylation of methane, the catalytic activity of Amavadine which we have already recognized to be able to display an haloperoxidase or peroxidase type activity in peroxidative halogenation, hydroxylation or oxygenation reactions of alkanes and aromatics [17], and may behave as an electron-transfer mediator in the catalytic oxidation of thiols [18,19].

### (c) Technical description

The invention concerns the utilization of systems, formed by complexes of vanadium (in the oxidation state +4 or +5) with di- or poly-dentate ligands coordinated by nitrogen and oxygen (*N,O*) or by oxygen (*O,O*) atoms, derived from aminoalcohols, (hydroxyimino)dicarboxylic acids, hydroxypyranones, trifluoroacetic acid, triflic acid or inorganic acids, as catalysts for the direct single-pot conversion of methane into acetic acid, either in the absence or in the presence of carbon monoxide, and in the presence of a peroxodisulfate salt ( $K_2S_2O_8$ ), in trifluoroacetic acid ( $CF_3COOH$ ), according to the general reaction (I).



Three main types of catalysts have been considered: (i) oxovanadium(V) complexes of the type  $[VO(N,O-L)]$  [ $N,O-L$  = basic form the triethanolamine  $N(CH_2CH_2O)_3$  or of  $N,N$ -bis(2-hydroxyethyl)glicine (bicine)  $N(CH_2CH_2O)_2(CH_2COO^-)$ ], (ii) the synthetic Amavadine and its models, namely the  $Ca^{2+}$  salts of the vanadium(IV) complexes, with  $N,O$  ligands,  $[V(HIDPA)_2]^{2-}$  [ $HIDPA$  = basic form of 2,2'-(hydroxyimino)dipropionic acid,  $ON\{CH(CH_3)COO^-\}_2$ ] and  $[V(HIDA)_2]^{2-}$  [ $HIDA$  = basic form of 2,2'-(hydroxyimino)diacetic acid,  $ON(CH_2COO^-)_2$ ], and (iii) the vanadium(IV) complexes with vanadyl and  $O,O$ -ligands of the type  $[VO(O,O-L)_2]$  [ $O,O-L$  = basic form (maltolate) of maltol (3-hydroxy-2-methyl-4-pyrone); dibasic form (heida) of 2-hydroxyethyliminodiacetic acid,  $N(CH_2CH_2OH)(CH_2COO^-)_2$ ; trifluoroacetate ( $CF_3COO^-$ ); triflate ( $CF_3SO_2O^-$ )] and  $VOSO_4$ .

Illustrative values for the turnover number (TON, moles of acetic acid per mol of metal catalyst) and for the yield (based on methane) are shown in the Table, for typical experimental conditions comprising  $CH_4$ :V catalyst and  $K_2S_2O_8$ :V catalyst molar ratios of 46:1 (corresponding to a  $CH_4$  pressure of 5 atm) and 200:1, respectively, in  $CF_3COOH$  at 80 °C. The values indicated have been obtained commonly after 20h reaction time, but often a much shorter period is sufficient to lead to a yield that is close to that observed after that time (e.g., entry 1 with an yield after 2h that is already 92% of that obtained after 20h).

– Table –

The most active catalysts (the yields, based on methane, can be above 50% and the TONs approach 30) are the following ones: the triethanolamine (basic form) complex  $[VO\{N(CH_2CH_2O)_3\}]$  within those of type (i), the Amavadine models (type ii) and, among those of type (iii),  $[VO(O,O-L)_2]$  ( $O,O-L$  = maltolate,  $CF_3COO^-$  or  $CF_3SO_2O^-$ ). In contrast,  $[VO(N,O-L)]$  ( $N,O-L$  = bicine or heida) and the simpler  $VOSO_4$  salt exhibit much lower activities.

The carboxylation of methane does not require the presence of carbon monoxide, although this gas can also act as a carbonylating agent (see below).

Methane constitutes the carbon source for the methyl group of acetic acid, as shown by the formation of  $^{13}CH_3COOH$ , identified by  $^{13}C-\{^1H\}$  and  $^{13}C$  NMR spectrometry, where using  $^{13}C$

enriched methane. The carbonyl group of this acid should be originated, in the absence of CO, from the solvent, CF<sub>3</sub>COOH, which is known [20] to react with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> derivatives in radical processes. The formation of acetic acid should not involve the conversion of methane into free methanol since this alcohol, under the experimental conditions used, is not converted into that acid.

CO can enhance the formation of acetic acid at sufficiently low pressures, suggesting that it can act as a carbonylating agent, but the effect can be minor, as observed for [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>}]. The use of higher CO pressures (*e.g.* above *ca.* 8 atm for this catalyst and for 5 atm pressure of methane) results in an inhibiting effect.

The change of methane pressure can affect markedly the TON which, for example, increases from 5 to 28 when that pressure increases from 3 to 12 atm in the case of the [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>}] catalyst. After reaching a maximum, the yield tends to decrease when the methane pressure increases.

Higher yields can be obtained by using (i) lower methane amounts for the same pressure – *e.g.* the yield increases from 17% to 54% upon decreasing that amount by a factor of 2.8, in the case of Ca[V(HIDPA)<sub>2</sub>] – or (ii) higher catalyst amounts – *e.g.* the yield increases from 24 to 43% with a fivefold increase of [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>}] concentration, at CO and CH<sub>4</sub> pressures of 5 atm.

In any of the cases studied, the reaction does not proceed in the absence of the vanadium catalyst.

### Examples

For illustrative purposes, the following description is presented for a typical experiment which can easily be adapted to other conditions:

The vanadium catalyst (0.0625 mmol) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.38 g, 12.5 mmol) are added to CF<sub>3</sub>COOH (23 cm<sup>3</sup>) contained in a 39 cm<sup>3</sup> stainless steel autoclave which is then closed. The air is removed by dinitrogen gas flow and vacuum, whereafter methane is introduced up to the required pressure (*e.g.* 5 atm, 2.86 mmol) and the autoclave is heated in an oil bath at the required temperature and for the required time, with stirring of the reaction mixture. After cooling the autoclave and venting the residual gases, the autoclave is opened and the solution in the final mixture is filtered. The excess of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is precipitated by addition of diethylether to the solution and

is removed by filtration. The resulting solution is then analysed by gas chromatography (GC) or by gas chromatography – mass spectrometry (GC-MS).

A similar procedure is followed for the essays in the presence of CO, in which this gas is admitted to the autoclave after the introduction of methane. The essays with different reagent molar ratios, volumes of solvent or different capacities autoclaves are performed similarly.

The following complexes were prepared according to literature methods: [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>} ] [21], Ca[V(HIDPA)<sub>2</sub>] [22], Ca[V(HIDA)<sub>2</sub>] [22], [VO(maltolate)<sub>2</sub>] [23] and [VO(CF<sub>3</sub>SO<sub>2</sub>O)<sub>2</sub>] [24]. The new complexes [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>(CH<sub>2</sub>COO)}], [VO{N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>COO)<sub>2</sub>}(H<sub>2</sub>O)] and [VO(CF<sub>3</sub>COO)<sub>2</sub>] were obtained by processes similar to those of [VO{N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>}], of ref. [25] or of [VO(CF<sub>3</sub>SO<sub>2</sub>O)<sub>2</sub>], respectively, but using the appropriate ligand. Compounds VOSO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and CF<sub>3</sub>COOH were purchase from Merck and Aldrich.

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Table. Conversion of methane into acetic acid (typical examples)<sup>a</sup>

Type (i)	Catalyst	p(CH <sub>4</sub> ) <sup>b</sup> (atm)	p(CO) <sup>b</sup> (atm)	Time (h)	TON <sup>c</sup>	Yield <sup>d</sup> (%)
$[\text{VO}\{\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\}]^e$						
	5	-	-	2	9	20
	5	-	-	20	10	21
	5	5	20	11	24	
	5	15	20	10	22	
	5	20	20	6	13	
	3	15	20	5	19	
	8	15	20	25	34	
	12	15	20	28	26	
	5	15	20	10 <sup>f</sup>	35 <sup>f</sup>	
	5	5	20	4 <sup>g</sup>	43 <sup>g</sup>	
$[\text{VO}\{\text{N}(\text{CH}_2\text{CH}_2\text{O})_n$ $(\text{CH}_2\text{COO})\}]^h$						
	5	-	-	20	2	5
Type (ii)						
$\text{Ca}[\text{V}(\text{HIDPA})_h]$						
	5	-	-	2	7	15
	5	-	-	20	13	29
	5	5	20	10	21	
	5	15	20	8	17	
	8	15	20	10	16	
	5	15	20	12 <sup>i</sup>	54 <sup>i</sup>	

Type (iii)	Ca[V(HIDA) <sub>2</sub> ] <sup>5</sup>								
[VO(malolate) <sub>2</sub> ] <sup>7</sup>	5	-	20	10	10	7	7	15	15
[VO{N(CH <sub>2</sub> CH <sub>2</sub> OH)(CH <sub>2</sub> COO) <sub>2</sub> }(H <sub>2</sub> O)] <sup>k</sup>	5	15	20	8	8	2	2	5	18
[VO(CF <sub>3</sub> COO) <sub>2</sub> ] <sup>7</sup>	5	-	20	20	20	2	2	4	21
[VO(CF <sub>3</sub> COO) <sub>2</sub> ] <sup>7</sup>	5	-	20	11	11	11	11	23	21
[VO(CF <sub>3</sub> SO <sub>2</sub> O) <sub>2</sub> ] <sup>7</sup>	5	20	20	9	9	9	9	19	19
[VO(CF <sub>3</sub> SO <sub>2</sub> O) <sub>2</sub> ] <sup>7</sup>	5	-	20	7	7	7	7	15	15
VOSO <sub>4</sub> <sup>m</sup>	5	5	20	10	10	10	10	22	22
VOSO <sub>4</sub> <sup>m</sup>	5	-	20	12	12	12	12	29	29
VOSO <sub>4</sub> <sup>m</sup>	5	20	20	1	1	2	2	2	5

<sup>a</sup> At the typical conditions mentioned in the experimental part and at 80 °C, unless stated otherwise.

<sup>b</sup> Pressure measured at 25 °C.

<sup>c</sup> Turnover number: moles of acetic acid per mol of metal catalyst.

<sup>d</sup> Molar yield (%) relatively to methane, *i.e.* moles of acetic acid per 100 moles of methane.

<sup>e</sup> *N,O*-ligand = basic form of triethanolamine.

<sup>f</sup> Relatively to <sup>a</sup>, a smaller amount of CH<sub>4</sub> was used (1.84 mmol), by using a greater volume of CF<sub>3</sub>COOH (28 cm<sup>3</sup>).

<sup>g</sup> Relatively to <sup>a</sup>, a fivefold amount of metal catalyst was used (0.312 mmol).

<sup>h</sup> *N,O*-ligand = basic form of *N,N*-bis(2-hydroxyethyl)glycine (bicine).

<sup>i</sup> Relatively to <sup>a</sup>, a smaller amount of methane (1.02 mmol) was used in a lower capacity reactor (23.5 cm<sup>3</sup>): metal catalyst (0.046 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (9.2 mmol, *i.e.* 200: 1 catalyst), CF<sub>3</sub>COOH (17 cm<sup>3</sup>).

<sup>j</sup> Maltolate = basic form of maltol (3-hydroxy-2-methyl-4-pyrone).

<sup>k</sup> *N,O*-ligand (heida) = dibasic form of 2-hydroxyethyliminodiacetic acid (complex molecule with one H<sub>2</sub>O of crystallisation).

<sup>l</sup> With 2H<sub>2</sub>O of crystallisation per complex molecule.

<sup>m</sup> With 5H<sub>2</sub>O per complex molecule.